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(54) AGENT ANTICORROSION EXEMPT DE CHROME ET PROCÉDE DE PROTECTION CONTRE LA CORROSION
(54) CHROMIUM-FREE CORROSION PROTECTION AGENT AND METHOD FOR PROVIDING CORROSION
PROTECTION

(57)

The invention relates to a chromium-free aqueous corrosion protection agent for treating galvanised or alloy galvanised steel surfaces or aluminium surfaces. Said agent contains the following essential constituents: a) 0.5 to 10 g/l hexafluoro-anions of titanium (IV) and/or zircon (IV), b) 5 to 15 g/l vanadium ions, c) 0.5 to 2 g/l transition metal ions, preferably Mn, Fe, Co, d) 30 to 150 g/l phosphoric acid and/or phosphonic acid. The inventive corrosion protection agent preferably also contains an organic film former, especially with a polyacrylate base; and a conductivity pigment. The agent is particularly suitable for treating metal strips in order to protect them against corrosion, with or without subsequent painting, and is preferably applied in such a way as to produce a dry layer coating of 0.5 to 5 g/m² on the surface.



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(54) **AGENT ANTICORROSION EXEMPT DE CHROME ET
PROCÉDE DE PROTECTION CONTRE LA CORROSION**

(54) **CHROMIUM-FREE CORROSION PROTECTION AGENT AND
METHOD FOR PROVIDING CORROSION PROTECTION**

(57) L'invention concerne un agent anticorrosion aqueux exempt de chrome s'utilisant pour traiter des surfaces en acier galvanisé ou galvanisé par alliage, ainsi qu'en aluminium. Cet agent contient comme principaux constituants: a) entre 0,5 et 10 g/l d'hexafluoro-anions de titane (IV) et/ou de zircon (IV), b) entre 5 et 15 g/l d'ions de vanadium, c) entre 0,5 et 2 g/l d'ions de métal de transition, de préférence Mn, Fe, Co, d) entre 30 et 150 g/l d'acide phosphorique et/ou d'acide phosphonique. Cet agent anticorrosion contient de préférence en outre un agent filmogène organique, notamment à base de polyacrylate. L'agent anticorrosion contient de plus de préférence un pigment de conductivité. Cet agent anticorrosion s'utilise notamment pour appliquer des traitements anticorrosion à de feuillards, avec ou sans laquage subséquent, et est appliqué de préférence de manière à obtenir sur la surface un revêtement à couche sèche comprise entre 0,5 et 5 g/m².

(57) The invention relates to a chromium-free aqueous corrosion protection agent for treating galvanised or alloy galvanised steel surfaces or aluminium surfaces. Said agent contains the following essential constituents: a) 0.5 to 10 g/l hexafluoro-anions of titanium (IV) and/or zircon (IV), b) 5 to 15 g/l vanadium ions, c) 0.5 to 2 g/l transition metal ions, preferably Mn, Fe, Co, d) 30 to 150 g/l phosphoric acid and/or phosphonic acid. The inventive corrosion protection agent preferably also contains an organic film former, especially with a polyacrylate base, and a conductivity pigment. The agent is particularly suitable for treating metal strips in order to protect them against corrosion, with or without subsequent painting, and is preferably applied in such a way as to produce a dry layer coating of 0.5 to 5 g/m² on the surface.



Abstract

**Chromium-free corrosion protective and
corrosion prevention process**

A chromium-free aqueous corrosion protective for treating surfaces of galvanised or alloy galvanised steel and of aluminum. It contains as the essential components:

- (a) from 0.5 to 10 g/l of hexafluoroanions of titanium(IV) and/or zirconium(IV);
 - (b) from 5 to 15 g/l of vanadium ions;
 - (c) from 0.5 to 2 g/l of cobalt ions;
- and
- (d) from 30 to 150 g/l of phosphoric acid:

The corrosion protective preferably also contains an organic film-forming component, particularly one based on polyacrylate. Furthermore, the corrosion protective preferably contains a conductive pigment. It is particularly suitable for corrosion preventive treatment of metal strips and is preferably applied in such a way that a dry-weight layer of from 0.5 to 5 g/m² is produced on the surfaces.

Chromium-free corrosion protective and corrosion prevention process

This invention relates to a chromium-free corrosion protective and a corrosion prevention process for treating surfaces of hot-dip galvanised or electrolytically galvanised steel, alloy galvanised steel or of aluminum and alloys thereof. It is particularly suitable for surface treatment using conveyor belt systems.

As a measure for temporary corrosion protection, galvanised or alloy galvanised steel strips, for example, are either simply oiled or they are phosphatised or chromatised when it is expected that they will be exposed to more severe corrosive conditions. In the case of very corrosive conditions, such as when transported by ship in salt-containing marine atmospheres or when stored in tropical environments, however, these measures are not adequate. The best temporary corrosion preventive measure disclosed in the prior art is a chromatising process in which the metal surfaces are coated with a chromium(III) and/or chromium(VI)-containing layer generally at a rate of about 5 to about 15 mg/m² of chromium. Due to the known toxicological problems of chromium compounds, this process is disadvantageous and costly from the point of view of occupational safety, ecology and the waste disposal measures which are required. In addition, chromatised sheet metal is less suitable for subsequent phosphatising since, on the one hand, it leads to chromium pollution of cleansing solutions and, on the other hand, the metal surfaces cannot generally be phosphatised over the whole area. Phosphatising as an alternative measure for the temporary corrosion protection may alter the appearance of the metal surfaces in an undesirable manner. In addition, a phosphatising process is costly in terms of equipment because, depending on the substrate material, an additional activating stage and generally a passivating stage after phosphatising are required. Passivating is frequently performed using chromium-containing treatment solutions, which also produces the previously-mentioned disadvantages associated with using chromium-containing treatment solutions.

To an increasing extent, metal strips are processed in the automobile and domestic appliance industries, and these strips have already been provided with a corrosion preventive layer by the manufacturer of the strips. These types of material are known, for example, under the names Durasteel⁷, Bonazinc⁷ and Durazinc⁷. They have a thin organic coating over a

conversion layer, for example a chromatising or phosphatising layer. The organic coating consists of polymer systems, such as epoxy or polyurethane resins, polyamides and polyacrylates. Solid additives such as silicas, zinc dust and carbon black, improve the corrosion protective effect and enable metal parts coated with layers having a thickness of about 0.3 to about 5 μm to be electrically welded and electrolytically lacquered due to the electrical conductivity thereof. Surface coating the substrate materials is generally performed in a two-stage process which is costly in terms of equipment, in which first the inorganic conversion layer is produced and then the organic polymer film is applied in a second treatment stage.

The prior art discloses trials using single-stage, surface coating processes in which the inorganic conversion treatment and surface coating with an organic polymer film are performed using a single treatment solution. US-A-5 344 504, for example, describes a surface coating process for galvanised steel in which the substrate is placed in contact with a treatment solution having the following composition: from 0.1 to 10 g/l of a tetra- or hexa-fluoroacid of boron, silicon, titanium and zirconium or hydrofluoric acid, about 0.015 to about 6 g/l of cations of cobalt, copper, iron, manganese, nickel, strontium or zinc and optionally up to about 3 g/l of a polymer selected from polyacrylic acid, polymethacrylic acid and esters thereof. The pH of this treatment solution is in the range from about 4 to about 5.

WO 95/14117 also describes a process for treating the surfaces of zinc or aluminium or alloys thereof. Here, the surfaces are placed in contact with a treatment solution having a pH of less than 3 which contains a complex formed from a metal oxyion and another ion. The metal oxyion is selected from molybdate, tungstate and vanadate. The other ion is selected from phosphorus, aluminium, silicon, manganese, magnesium, zirconium, titanium, tin, cerium and nickel. Furthermore, the treatment solution contains an organic film-forming component which is compatible with the other components in the solution. Polyacrylates, such as in particular polymers of methyl methacrylate, n-butyl acrylate, hydroxyethyl acrylate and glycerinepropoxy triacrylate, for example, are suitable as film-forming components.

EP-A-694 593 recommends the treatment of metal surfaces with a treatment solution which contains the following components: an organic polymer or copolymer in which from 0.5 to 8

% of the monomeric groups are able to form compounds with metal ions, complex cations or anions of aluminum, calcium, cerium, cobalt, molybdenum, silicon, vanadium, zirconium, titanium, trivalent chromium and zinc, an oxidising agent, such as nitric acid, perchloric acid or hydrogen peroxide, and an acid, such as oxalic acid, acetic acid, boric acid, phosphoric acid, sulfuric acid, nitric acid or hydrochloric acid.

WO 95/04169 discloses the treatment of metal surfaces with a treatment solution which contains at least the following components: fluorine complexes of titanium, zirconium, hafnium, silicon, aluminum and boron, metal ions selected from cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron and strontium, phosphates or phosphonates and water-soluble or water-dispersible organic film-forming components.

EP-A-792 922 describes a chromium-free corrosion inhibiting coating composition which contains a film-forming organic polymer and (i) a salt selected from the esters of rare-earth metals and alkali metal or alkaline earth metal vanadates and also (ii) a borate salt of an alkaline earth metal. The following are mentioned as preferred polymers, for example: epoxides including polyimide-based epoxides, polyurethanes, acrylic polymers and alkyd-based systems. This surface coating composition must therefore contain at least a borate and a further component, which may be a vanadate, in addition to the organic film-forming component.

Despite the prior art, there is still a need for improved surface coating processes for metal surfaces in which at least one inorganic passivating layer and preferably an organic polymer layer are applied to the metal surface in the same treatment step. The coating should facilitate the punching out and shaping of structural parts made from the coated metal strips. Furthermore, the layers should be able to withstand, undamaged, conventional treatment steps, such as cleansing and phosphatising, which are performed after assembling the products, for example car bodies or domestic appliances and be directly over-lacquerable. In order to protect the environment and for occupational safety reasons, it should be possible to perform the treatment process without using chromium compounds and if possible, also without using organic solvents.

The present invention relates to a chromium-free corrosion protective containing water and:

- (a) from 0.5 to 10 g/l of hexafluoroanions of titanium(IV) and/or zirconium(IV);
- (b) from 5 to 15 g/l of vanadium ions;
- (c) from 0.5 to 2 g/l of cobalt ions;
- (d) from 30 to 150 g/l of phosphoric acid;
- and
- (e) optionally other active or auxiliary substances.

Preferred concentration ranges for components (a) to (c) are:

- (a) from 1 to 3 g/l of hexafluoroanions of titanium(IV) and/or zirconium(IV);
- (b) from 6 to 10 g/l of vanadium ions;
- (c) from 0.6 to 1.2 g/l of cobalt ions.

The pH of the corrosion protective is in the range from 0.5 to 2.5, preferably in the range from 1.0 to 2.1 and in particular in the range from 1.4 to 2.0. An agent of this type dissolves the metal surfaces so that a working treatment bath may also contain additional cations which are produced from the substrates being treated. Examples of this are zinc and aluminum, as well as optionally other alloy components, such as iron, nickel and copper.

A person skilled in the art would recognise that the previously-mentioned components may enter into reactions with each other and that they are present in the treatment solution in forms which are stable under the conditions mentioned for pH. For example, hexafluoroanions are sometimes present in the form of the free acids. Vanadium ions are mostly present as VO_2^+ cations, but may also sometimes condense to produce polycations.

The corrosion protective may also contain other auxiliary or active substances. For example it may contain, as a further active substance, about 0.5 to about 10 g/l, in particular about 1 to about 5 g/l of non-complexed fluoride ions. These may be introduced as hydrofluoric acid or as a soluble fluoride, such as an alkali metal or ammonium fluoride. Independently of the compound used, the fluoride ions are largely present as undissociated hydrofluoric acid at the pH of the corrosion protective.

Furthermore, the corrosion protective may also contain about 1 to about 30 g/l, in particular about 10 to about 25 g/l, of a conductive pigment as a further active substance. This improves the ability of the substrate treated with the corrosion protective to be electrically welded and electrolytically lacquered. Suitable conductive pigments are, for example: carbon black, graphite, molybdenum sulfide, barium sulfate doped with tin or antimony and iron phosphide. Iron phosphide (Ferrophos, Fe_2P) is particularly preferred. It is preferably used in amounts of about 20 g/l.

The corrosion protective may also contain about 0.5 to about 50 g/l of polyethylene wax as a further active substance. The wax makes the coating slippery and thus improves the forming behavior of the substrates treated with the corrosion protective. This means that it is not necessary to apply forming oils to the surfaces during forming processes.

The corrosion protective also preferably contains about 15 to about 200 g/l, in particular about 50 to about 150 g/l of an organic film-forming component. A mixed inorganic/organic coating is therefore produced on the treated metal surfaces during use of the corrosion protective and this performs the function of a primer as well as that of a corrosion protective. The pre-treated metal parts may therefore be directly over-lacquered. Independently of that, the organic film-forming component also prevents constituents in the anti-corrosion layer formed by the effect of the corrosion protective being leached out during subsequent cleansing processes. In combination with the polyethylene wax, the organic film-former also improves the forming behavior.

The organic film-forming component may be selected, for example, from epoxide resins, polyurethane resins and polymers or copolymers of styrene, butadiene, acrylic acid, methacrylic acid and/or maleic acid and esters of these acids or from precursors of these polymers. Film-forming components which cross-link at a temperature below 180°C and in particular below 170°C are preferred. The organic film-former may be dissolved or dispersed in the corrosion protective. One example of this is an aqueous mixture of sodium polyacrylate and polyacrylic acid which is obtainable commercially having a solids content of 51 wt. % and a pH in the range from 2 to 3. Film-forming components based on acrylic acid and/or methacrylic acid and esters thereof with alcohols containing 1 to about 6 carbon atoms are

preferred. These polymers or copolymers preferably have a glass transition temperature in the range from 20 to 25°C.

Furthermore, the organic film-former may be an epoxide resin which may be formulated as a single component having an integrated hardener or as two components having a separate hardener. Water-dilutable systems are preferably chosen for these. Amines or polyamines are particularly suitable as hardeners for epoxide resins. Epoxide resins are generally commercially available as aqueous dispersions having resin contents in the range between about 50 and about 60 %. These dispersions generally contain small amounts of organic solvent, such as isopropanol or methoxypropanol. Furthermore, they generally contain an emulsifier which may also be fused directly to the epoxide resin. If these types of two-component epoxide resin systems are used in the context of the present invention, the epoxide dispersion mixed with the inorganic corrosion protective components, on the one hand, and the hardener component, on the other hand, may be stored in two separate containers and transported to the site of use. The two components are then mixed with each other shortly before application. An alternative to these types of two-component formulations are single-component epoxide resin systems which contain an integrated hardener. The integrated hardener may be, for example, an amine adduct which releases a free amine only when heated and this then initiates the hardening process.

The corrosion protective may also contain about 0.5 to about 2 wt.% of a silane-based adhesion promoter as a further active or auxiliary substance. Examples of these are aminopropyltriethoxysilane and glycidoxypopyl-trimethoxysilane.

The present invention also relates to a process for corrosion preventive treatment of surfaces of galvanised or alloy galvanised steel or of aluminum or alloys thereof, characterised in that the surfaces are contacted with a corrosion protective according to the present invention as described above for a period in the range from 2 to 60 seconds and then dried with or without intermediate washing with water at a substrate temperature (peak metal temperature) in the range from 50 to 180°C.

The process may thus be used, on the one hand, on galvanised or alloy galvanised steel. The

steel may have been coated with zinc or a zinc alloy in an electrolytic or hot-dip process. Suitable zinc alloys are in particular zinc/nickel, zinc/iron and zinc/aluminum alloys. On the other hand, the process is also suitable for treating surfaces of aluminum or alloys thereof. Aluminum alloys rather than pure aluminum are generally used in the automobile and domestic appliance industries. The most important alloying components are zinc, magnesium, silicon and copper.

The process is particularly suitable for treating metal strips on conveyor belt systems. The exposure time to the treatment agent, up to the start of the drying process, may then be in the region of a few seconds, for example between about 2 and about 20, and in particular between about 4 and about 12 seconds. The corrosion protective may be applied to the metal surfaces using a variety of methods known from the prior art. For example, the corrosion protective may be sprayed on to the metal surfaces or the surfaces may be wetted by immersion in the treatment agent. In both cases, it is advisable to use excess treatment solution to give a predetermined wet-film application which leads to the desired dry-weight application of about 0.5 to about 5 g/m² and in particular about 0.8 to about 3 g/m². The corrosion protective is preferably applied to the metal strips using application rollers similar to those known, for example, as Chemcoaters. The thickness of the wet-film may be directly adjusted when using these. In all cases, the corrosion protective remains on the strip at the desired wet-film thickness and is dried on without an intermediate washing process. Drying is performed in pre-heated furnaces or by the effect of infra-red radiation in such a way that the substrate reaches a temperature (peak metal temperature) in the range from about 50 to about 180°C and in particular in the range from about 100 to about 170°C. The optionally-used organic film-former is cured during this process.

If treatment according to the present invention is performed directly after electrolytic galvanising or hot-dip galvanising of the steel strips, then the strips may be placed in contact with the treatment solution according to the present invention without any further cleansing. However, if the metal strips to be treated have been stored and/or transported before being coated according to the present invention, then they have generally been provided with corrosion protective oils or at least have become so contaminated that cleansing is required prior to treatment according to the present invention. This may be performed using weak to

strong alkaline cleansers which are known from the prior art; in the case of aluminum and alloys thereof, acid cleansers may also be used.

Examples

Table 1 contains examples of corrosion protectives according to the present invention. They were prepared by mixing the individual components in the sequence given at room temperature. Sheet metal made from hot-dip galvanised and electrically galvanised steel was used as substrate. The sheets were cleansed prior to treatment with the corrosion protective using a commercial strongly alkaline cleanser. The solution was applied to the metal surfaces using a lacquering machine operating at 550 rpm. The exposure time up the beginning of drying was 15 seconds. Drying/firing of the coating was performed at a substrate temperature (?peak metal temperature?) of 100°C. For this purpose the coated sheets were placed in a circulating air cabinet heated to 300°C for 20 seconds.

Some of the treated test sheets were subjected to a salt spray test according to DIN 5002155 without further lacquering. After a test period of 48 hours, the corrosion on each of the three test sheets treated in the same way was assessed visually. Sheets without corrosion were given the score zero, sheets with more than 50 % corrosion the score 5. The results are given in Table 2.

Table 1: Composition of the corrosion protectives (parts, by weight)

Example number	Deionised water	ZnO	H ₃ PO ₄ (75%)	H ₂ MP ₆	HF (40 %)	NaVO ₃ (90%)	CoSO ₄ ·7H ₂ O	Film-former ^{b)}	pH
1	83.1	0.5	9.33	H ₂ TiF ₆ (50%) 0.8	0.44	2.2	3.63	-	1.2
2	83.29	-	9.33	H ₂ ZrF ₆ (50%) 1.11	0.44	2.2	3.63	-	1.1
3	82.79	0.5	9.33	H ₂ ZrF ₆ (50%) 1.11	0.44	2.2	3.63	-	1.2
4	61.04	0.5	9.33	H ₂ ZrF ₆ (50%) 1.11	0.44	2.2	3.63	21.75 ^{a)}	1.9
5	61.35	0.5	9.33	H ₂ ZrF ₆ (50%) 0.8	0.44	2.2	3.63	21.75 ^{a)}	1.6
6	82.79	0.5	9.33	H ₂ ZrF ₆ (50%) 1.11	0.44	2.2	3.63	-	1.2
7	52.14	0.45	8.4	H ₂ TiF ₆ (50%) 0.72	0.4	2	3.27	32.62	1.2
8	42.98	0.4	7.46	H ₂ TiF ₆ (50%) 0.64	0.35	1.76	2.9	43.5	1.2
9	63.01	0.45	8.4	H ₂ TiF ₆ (50%) 0.72	0.4	2	3.27	21.75 ^{a)}	1.1
10	64.74	0.4	7.46	H ₂ TiF ₆ (50%) 0.64	0.35	1.76	2.9	21.75 ^{a)}	1.2
11	55.75	0.5	9.33	H ₂ TiF ₆ (50%) 0.4	0.4	2.2	3.63	21.75 ^{a)}	2
	additional component: 1 part, by weight, of aminopropyltriethoxysilane								

- (1) Aqueous dispersion of a copolymer of esters of alcohols having from 1 to 6 carbon atoms and acrylic acid and methacrylic acids, 46 % solids
- (2) Corresponds to 10 parts, by weight, of solid with respect to the total formulation

Table 2: Corrosion preventive effect (degree of corrosion after a 48-hour salt spraying test)

Solution from example no.	Substrate ¹⁾	Degree of corrosion (3 sheets)		
1	HDG	1	1	1
2	HDG	0	1	0
3	HDG	0	0	0
6	HDG	1	1	0
6	EG	1	0	0
1	EG	0	0	0
4	EG	0	0	0
5	EG	0	0	0
7	EG	0	0	0
8	EG	0	0	0
9	EG	0	0	0
10	EG	0	1	1
11	EG	0	0	0

1) HDG = hot-dip galvanised steel

EG = electrolytically galvanised steel

Claims:

1. A chromium-free corrosion protective containing water and:
 - (a) from 0.5 to 10 g/l of hexafluoroanions of titanium(IV) and/or zirconium(IV);
 - (b) from 5 to 15 g/l of vanadium ions;
 - (c) from 0.5 to 2 g/l of cobalt ions;
 - (d) from 30 to 150 g/l of phosphoric acid;and
 - (e) optionally other active or auxiliary substances.
 2. A corrosion protective as claimed in claim 1 wherein it contains from 0.5 to 10 g/l of non-complexed fluoride ions as a further active substance.
 3. A corrosion protective as claimed in one or both of claims 1 and 2 wherein it also contains from 1 to 30 g/l of a conductive pigment as a further active substance.
 4. A corrosion protective as claimed in claim 3 wherein the conductive pigment is selected from carbon black, graphite, molybdenum sulfide, doped barium sulfate and iron phosphide.
 5. A corrosion protective as claimed in one or more of claims 1 to 4 wherein it also contains from 0.5 to 50 g/l of polyethylene wax as a further active substance.
 6. A corrosion protective as claimed in one or more of claims 1 to 5 wherein it also contains from 15 to 200 g/l of an organic film-forming component as a further active substance.
 7. A corrosion protective as claimed in claim 6 wherein the organic film-former is selected from epoxide resins, polyurethane resins and polymers or copolymers of styrene, butadiene, acrylic acid, methacrylic acid and/or maleic acid and esters of these acids.
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8. A corrosion protective as claimed in claim 7 wherein the organic film-former is a copolymer of esters of acrylic acid and methacrylic acid with alcohols containing 1 to 6 carbon atoms.
9. A corrosion protective as claimed in one or more of claims 1 to 8 wherein it has a pH in the range from 0.5 to 2.5.
10. A process for the corrosion preventive treatment of surfaces of galvanised or alloy galvanised steel or of aluminum or alloys thereof, characterised in that the surfaces are contacted with a corrosion protective as claimed in one or more of claims 1 to 10 for a period in the range from 2 to 60 seconds and is then dried at a substrate temperature in the range 50 to 180°C without intermediate washing with water.
11. A process as claimed in claim 10 wherein a dry-weight layer of from 0.5 to 5 g/m² is produced on the surfaces.